

Summary.

1. This study confirms earlier work which has shown that the permanganate titration of ferrous iron in the presence of fluorides gives an unstable end point, the instability increasing with increased concentrations of iron and hydrofluoric acid.

2. The use of sulfuric acid of normal to 5 *N* concentrations permits a good titration to be made in the presence of normal hydrofluoric acid. Phosphoric acid can not be substituted for sulfuric acid, since the former yields a fugitive end point. Certain acid sulfates accomplish the same result as the free acid.

3. Certain sulfates, *i. e.*, ferric and magnesium sulfates, react with the hydrofluoric acid and check its influence in the titration. Phosphates and acid phosphates are undesirable for prevention of the fluoride influence.

4. Certain oxides also have prevention tendencies, *i. e.*, molybdenum trioxide and titanium dioxide, the titanium dioxide being the better. The hydrofluoric acid may combine with the titanium and molybdenum, forming simple fluorides or fluotitanic and fluomolybdic acids. Boric acid and silicic acid remove the hydrofluoric acid, forming fluoboric and fluosilicic acids. Boric acid is the most effective of all reagents studied.

5. Ferrous iron solutions containing fluoboric acid are quite stable in the presence of air.

6. The prevention of the reagents studied may be classified in three divisions: (1) addition of a stronger acid than hydrofluoric acid for the solution medium, (2) conversion to salts of other acids forming also undissociated or sparingly dissociated fluorides by mass action of the preventer, and (3) conversion of the hydrofluoric acid to a complex acid which when dissociated, gives a complex anion rather than the simple fluorine ion.

7. A modified procedure is given for the analysis of silicate or carbonate rocks for their ferrous iron content, using boric acid to remove the detrimental influence of the hydrofluoric acid.

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THE PERMANGANATE AND IODIMETRIC DETERMINATION OF IODIDE IN PRESENCE OF CHLORIDE AND BROMIDE.¹

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The permanganate oxidation of iodide to iodate originated with Pean de Saint Gilles.² A large number of modifications of this method have

¹ Read at the New Orleans meeting of the American Chemical Society.

² Pean de Saint Gilles, *Compt. rend.*, 46, 624 (1858).

been made but they still retain the fundamental idea of conversion of iodide to iodate. Certain authors use other oxidizing agents, such as nickelic oxide,¹ potassium dichromate,² chlorine³ to accomplish the same purpose.

Theoretically this reaction has many points in its favor, the essential one being its application to the estimation of small quantities of iodides. For this purpose the addition of three oxygen atoms to the iodide demands a sufficiently large quantity of oxidizing agent to make the titration quite accurate. The measure of the amount of oxidizing agent required or of the iodate formed gives two means for the quantitative determination of iodides.

Pean de Saint Gilles⁴ determined the quantity of iodide by adding an excess of permanganate to the neutral or alkaline solution, heating a few minutes, adding an excess of ferrous sulfate containing sulfuric acid and then titrating the excess of ferrous iron remaining in the solution. Hence the original method consists of a measure of the oxidation of iodide to iodate from the quantity of permanganate required. Klemp⁵ adds zinc chloride to facilitate precipitation of the manganese and watches for the appearance of the permanganate color in the supernatant liquid. The end point is obscure, however, and continuous heating and cautious addition of permanganate is required to obtain even a moderately good result. Reinige⁶ determined the excess of permanganate with sodium thiosulfate. Sonstadt⁷ precipitates the iodic acid formed by this reaction with barium chloride, transforms the barium iodate with potassium sulfate to potassium iodate and then estimates the amount of iodate "either gravimetrically or iodimetrically." Other investigators have destroyed the excess of permanganate with such agents as alcohol⁸ or hydrogen peroxide,⁹ filtered out the hydrated manganese dioxide and then titrated the iodic acid in the filtrate iodimetrically. Sodium sulfite¹⁰ has been used to reduce the permanganate, later reducing iodic to hydriodic acid and converting to silver iodide. McCullock¹¹ pointed out that the measure

¹ McCullock, *Chem. News*, **57**, 45 (1888).

² Baubigny and Chavanne, *Compt. rend.*, **136**, 1197 (1903); *Chem. Zig.*, **28**, 555 (1903); Emde, *Ibid.*, **35**, 450 (1911).

³ Hunter, *J. Biol. Chem.*, **7**, 321 (1910); *Proc. Soc. Exp. Biol. Med.*, **7**, 10 (1910); Kendall, *THIS JOURNAL*, **34**, 894 (1912).

⁴ Pean de Saint Gilles, *Compt. rend.*, **46**, 624 (1858).

⁵ Klemp, *Z. anal. Chem.*, **20**, 248 (1881).

⁶ Reinige, *Ibid.*, **9**, 39 (1870).

⁷ Sonstadt, *Chem. News*, **26**, 173 (1872).

⁸ Gröger, *Z. angew. Chem.*, **7**, 52 (1894); Longi and Bonavia, *Gazz. chim. ital.*, **28**, 325 (1898); Bernier and Peron, *J. pharm. chim.*, **3**, 242 (1911); **4**, 151 (1911); Knudsen, *Chem. Eng.*, **17**, 119 (1913).

⁹ Auger, *Bull. soc. chim.*, **11**, 615 (1912).

¹⁰ Baubigny and Rivals, *Compt. rend.*, **137**, 927 (1903).

¹¹ McCullock, *Chem. News*, **57**, 45, 135 (1888). McCullock also titrates iodide in presence of cyanide in sulfuric acid solution with permanganate, converting the iodide to iodine cyanide. In presence of strong hydrochloric acid titration yields ICl; hydrobromic acid yields BrI.

of the available oxygen from the hydrated manganese precipitate gives erroneous results, inasmuch as the precipitate is not pure manganese dioxide, but contains some manganous manganese. This condition of mixed oxides is one that might be anticipated from the general chemistry of the oxides of manganese. The oxide precipitated by the interaction of a reducing agent on permanganate or manganate or by an oxidizing agent on manganous manganese almost, if not invariably, contains part of its manganese in a lower state of oxidation than four.¹ The titration of iodic acid iodimetrically with thiosulfate, after removal of the excess of permanganate by alcohol or similar reducing agent and subsequent removal of the resulting manganese dioxide by filtration, removes the difficulty of an inconstant manganese oxide product of reaction and lessens filtration troubles, inasmuch as a considerable excess of permanganate can be employed and heating continued, if necessary, until the solution is quite easily filtered. The use of hydrogen peroxide² or alkali sulfites³ for the removal of the excess of permanganate would necessitate great care to avoid reduction of an appreciable amount of iodate, as these reducing agents are used to effect quantitative reduction of iodate to iodide.

Investigators using chlorine or hypochlorite have removed the excess of oxidizing agent by means of a current of air,⁴ boiling,⁵ or phenol.⁶ However, the general idea remains the same, conversion of the iodide to iodate and ascertaining the quantity of iodate formed.

The investigation to be outlined in the following pages is divided into two parts: (1) the permanganate titration according to the original and modified method of Pean de Saint Gilles and (2) the iodimetric titration of the iodate formed by the permanganate oxidation of the iodide.

1. The Permanganate Titration of Iodides.

The success or failure of the permanganate method as outlined by Pean de St. Gilles is dependent for the most part on the quantitative oxidation of ferrous to ferric iron by the permanganate in the presence of chloride and bromide. When the titration of ferrous iron with permanganate is attempted in the presence of halides in acid solution free halogen is liberated, the ease with which this liberation occurs increasing in the order hydrochloric, hydrobromic and hydriodic acids. The effect of chlorides

¹ J. Volhard, *Ann. Chem. Pharm.*, **198**, 318 (1879); Meineke, *Rep. d. anal. Chem.*, **3**, 337 (1883); **5**, 1 (1885); Hintz, *Z. anal. Chem.*, **24**, 421 (1885); Weber, *Ibid.*, **43**, 564, 643 (1904).

² Lenssen, *J. prakt. Chem.*, **81**, 276 (1860); Jannasch and Aschoff, *Z. anorg. Chem.*, **1**, 144, 245 (1892); **5**, 8 (1894).

³ Emde, *Chem. Ztg.*, **35**, 450 (1911).

⁴ Gil, *Rev. real. acad. cien.*, Madrid, **8**, 272; *Chem. Abst.*, **4**, 2616 (1910).

⁵ Hunter, *Loc. cit.*

⁶ Kendall, *Ibid.*

has been studied by a number of investigators¹ and various reagents have been used to prevent the detrimental influence of chlorides. Manganous salts have been found to be particularly effective. The author finds that manganous salts² also prevent the evolution of bromine, the best results being obtained in phosphoric acid solution.

If an alkaline solution containing chloride or bromide and permanganate is treated with ferrous sulfate acidified with sulfuric acid, chlorine (or hypochlorous acid) or bromine is liberated. If the acid ferrous sulfate solution is added in sufficient quantity all at once, thus insuring acidity only when the iron solution can give reduction at the same instant as acidity, then the liberation of halogen is greatly diminished. However, if sufficient manganous sulfate is added to the ferrous sulfate solution, which contains phosphoric acid, before the ferrous iron solution is added to the permanganate solution, then the tendency toward halogen liberation can be completely eliminated. The ferrous iron in the resulting solution can then be titrated accurately with permanganate.

Several series of analyses, in which the time of heating the iodide with permanganate was studied, showed that the heating should be continued a few minutes after the solution reached boiling temperature. Five minutes sufficed in every case. The effect of varying alkalinity was also tried and a low concentration of alkali found to give the best results. In acid solutions free iodine is liberated, which is transposed to iodic acid in part. If the concentration of acid is low, some iodine is liberated, complete conversion to free iodine being effected when the acid attains sufficient strength. In neutral solution the transposition is complete to iodic acid, but more time is required than in alkaline solution. Inasmuch as strong alkaline solutions of permanganate on heating decompose to a greater or less extent, liberating oxygen, a 0.01 *N* solution of sodium hydroxide was chosen for this work, 1 cc. of normal alkali being added for each 100 cc. of solution present. Heating just below boiling for five minutes a 0.01 *N* sodium hydroxide solution containing a moderate amount of permanganate (10–20 cc. of 0.1 *N* solution) causes a loss of oxygen which is so small as to be negligible. In fact such solutions give very little loss when heated for sixty minutes.

When a considerable quantity of iodic acid is treated with a large excess of ferrous iron in acid solution more or less reduction of the iodate occurs, simultaneously oxidizing the iron and liberating free iodine. To ascertain the extent of the reducing effect of ferrous iron on iodic acid in the presence of varying concentrations of sulfuric and phosphoric acids, a series of experiments was performed (Table I). In this series the quantity of potassium iodate was kept constant throughout and the other

¹ See Barnebey, *THIS JOURNAL*, 36, 1429 (1914).

² See also Phelps, *Am. J. Sci.*, 17, 201 (1904).

factors varied in a systematic manner. Each experiment was performed at room temperature. Each solution was allowed to stand 5 minutes after mixing the reagents. The volume before titration was 200 cc. in each case.

TABLE I.—REDUCTION OF IODIC ACID BY FERROUS SULFATE.

1 cc. $\text{KMnO}_4 = 0.009208$ g. Fe.

1 cc. $\text{FeSO}_4 = 0.658$ cc. KMnO_4 .

50 cc. of 0.1 N KIO_3 (3.5678 g. per liter) used in each experiment.

Normality.		Iron—Gram.			Normality.		Iron—Gram.		
H_2SO_4 .	H_3PO_4 . ¹	Present.	Found.	Error.	H_2SO_4 .	H_3PO_4 . ¹	Present.	Found.	Error.
0.5	...	0.0606	0.0608	+0.0002	...	1.0	0.0606	0.0610	+0.0004
0.5	...	0.1212	0.1213	+0.0001	...	1.0	0.1212	0.1212	0.0000
0.5	...	0.1818	0.1818	0.0000	...	1.0	0.1818	0.1812	-0.0006
0.5	...	0.2424	0.2422	-0.0002	...	1.0	0.2424	0.2410	-0.0014
0.5	...	0.3030	0.3029	-0.0001	...	1.0	0.3030	0.3011	-0.0019
...	0.5	0.0606	0.0606	0.0000	1.5	...	0.0606	0.0608	+0.0002
...	0.5	0.1212	0.1213	+0.0001	1.5	...	0.1212	0.1208	-0.0004
...	0.5	0.1818	0.1818	0.0000	1.5	...	0.1818	0.1812	-0.0006
...	0.5	0.2424	0.2420	-0.0004	...	1.5	0.0606	0.0608	+0.0002
...	0.5	0.3030	0.3029	-0.0001	...	1.5	0.1212	0.1210	-0.0002
1.0	...	0.0606	0.0608	+0.0002	...	1.5	0.1818	0.1812	-0.0006
1.0	...	0.1212	0.1212	0.0000	2.5	...	0.0606	0.0608	+0.0002
1.0	...	0.1818	0.1814	-0.0004	2.5	...	0.1212	0.1197	-0.0015
1.0	...	0.2424	0.2414	-0.0010	...	2.5	0.0606	0.0608	+0.0002
1.0	...	0.3030	0.3011	-0.0019	...	2.5	0.1212	0.1200	-0.0012

All the low results of this series were caused by a partial oxidation of ferrous iron by the iodic acid, more or less iodine being visible at the end of the five-minute period preceding titration. In no case was iodine liberated at once. These results indicate that the solution should not have an acidity with sulfuric or phosphoric acid greater than normal and that not more than 0.1 g. of ferrous iron should be added in excess, if five minutes are to be allowed to intervene between the time of adding the excess of iron salt and titration of that excess with permanganate. However, much larger quantities of both ferrous iron and sulfuric or phosphoric acids can be present if the excess of ferrous iron is titrated immediately.

Table II gives the results of actual analyses of known amounts of potassium iodide, thus showing the combined effect of manganese dioxide and potassium iodate on the decomposition of potassium permanganate and also obtaining a further check on the reduction of iodic acid by ferrous iron. The potassium iodide was measured into an Erlenmeyer flask, and 1 cc. of N NaOH added, followed by the permanganate. The solution was heated to boiling and kept just below ebullition for the time designated. After cooling in running water the mixed solution of 50 cc. of

Computed on the basis of three replaceable H atoms.

ferrous sulfate (1 cc. = 0.802 cc. KMnO_4) plus 25 cc. of manganese preventive solution (60 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and 250 cc. H_3PO_4 of sp. gr. 1.70 per liter) was added. The time interval of standing previous to titration was about ten minutes in each experiment. No iodine was visible before titration, which showed that no reduction of iodic acid had taken place.

TABLE II.—PERMANGANATE DETERMINATION OF IODIDE IN PURE POTASSIUM IODIDE.

1 cc. KMnO_4 = 0.005648 g. Fe = 0.002798 g. KI.
 1 cc. KMnO_4 = 0.8020 cc. FeSO_4 .
 0.01 N KI = 1.66 g. KI per liter.

	0.01 N KI. Cc.	KMnO_4 . Cc.	Time. Min.	KMnO_4 required for excess. Cc.	KMnO_4 required for FeSO_4 . Cc.	KMnO_4 required for KI. Cc.	G. KI.	
							Present.	Found.
1.....	50	60	5	9.60	40.10	29.50	0.0830	0.0825
2.....	50	60	15	9.64	40.10	29.54	0.0830	0.0827
3.....	50	60	30	9.64	40.10	29.54	0.0830	0.0827
4.....	50	60	60	9.64	40.10	29.54	0.0830	0.0827

The two preceding tables of results allow at least three conclusions: (a) the loss due to heating of the alkaline solution is negligible, (b) the reducing action of ferrous iron on the iodic acid can be made inappreciable, and (c) accurate determinations of iodide can be made by using the mixed solution containing some manganese salt and ferrous sulfate to remove the excess of permanganate as well as the hydrated manganese dioxide, the excess of ferrous iron being subsequently titrated with permanganate.

TABLE III.—PERMANGANATE DETERMINATION OF IODIDE IN MIXTURES WITH CHLORIDE AND BROMIDE.

1 cc. KMnO_4 = 0.005648 g. Fe.
 1 cc. KMnO_4 = 0.8275 cc. FeSO_4 .
 1 cc. KI = 0.00166 g. KI.

	0.1 N KBr. Cc.	0.1 N NaCl. Cc.	MnSO_4 . Cc.	H_3PO_4 . Cc.	KI—Gram.		
					Present.	Found.	Error.
1.....	10	..	10	15	0.0830	0.0828	—0.0002
2.....	30	..	10	15	0.0830	0.0827	—0.0003
3.....	60	..	10	15	0.0830	0.0828	—0.0002
4.....	100	..	10	15	0.0830	0.0831	+0.0001
5.....	5 g. KBr.	..	10	15	0.0830	0.0828	—0.0002
6.....	10 " "	..	50	15	0.0830	0.0838	+0.0008
7.....	20 " "	..	100	25	0.0830	0.0827	—0.0003
8.....	..	50	10	15	0.0830	0.0827	—0.0003
9.....	..	10 g. NaCl	50	25	0.0830	0.0827	—0.0003
10.....	50	50	10	15	0.0017	0.0018	+0.0001
11.....	50	50	10	15	0.0033	0.0035	+0.0002
12.....	50	50	10	15	0.0083	0.0086	+0.0003
13.....	50	50	10	15	0.0166	0.0168	+0.0002
14.....	50	50	10	15	0.0415	0.0414	—0.0001
15.....	50	50	10	15	0.0830	0.0827	—0.0003

In Series III 50 cc. portions of 0.01 *N* potassium iodide solution were treated in an Erlenmeyer flask with permanganate in excess in the presence of bromides and chlorides, added in the form of 0.1 *N* potassium bromide and 0.2 *N* sodium chloride, or of the solids. One cc. of *N* sodium hydroxide was added, the solution heated and potassium permanganate added until there was about 10 cc. excess, then the solution was heated for about five minutes. The solution was cooled, and the ferrous sulfate solution (containing 250 g. per liter of manganous sulfate) was added in sufficient quantity to be about 10 cc. in excess. After complete solution of the manganese dioxide, phosphoric acid (1:3) was added. The excess of ferrous iron was then titrated with the permanganate.

In sample 6 the end point was blurred because of liberation of free bromine, the odor of which was distinct. $MnSO_4$ was not present in sufficient amount to take care of the large amount of KBr added originally. In other titrations concordant results were obtained.

In Series IV, 0.001 *N* potassium iodide was used with 0.001 *N* permanganate and 0.001 *N* ferrous sulfate. The method of procedure was the same as with 0.01 *N* potassium iodide. 1 cc. of *N* sodium hydroxide and 5 cc. of preventive solution (200 g. $MnSO_4 \cdot 4H_2O$ and 350 cc. H_3PO_4 of sp. gr. 1.7 per liter) were employed in each case. The total volume was 100 cc. for each titration. Considerable care was found to be necessary to exclude foreign impurities when dealing with such weak solutions of permanganate. Only recently boiled water, previously distilled from alkaline permanganate, was employed. The titrations were continued carefully to the first definite pink color and the amount of permanganate necessary to give the same pink color in a blank experiment was subtracted.

TABLE IV.—PERMANGANATE DETERMINATION OF SMALL AMOUNTS OF IODIDE IN HALIDE MIXTURES.

	0.1 <i>N</i> KBr. Cc.	0.1 <i>N</i> NaCl. Cc.	KI—Gram.		
			Present.	Found.	Error.
1.....	5	5	0.00017	0.00016	—0.00001
2.....	5	5	0.00033	0.00033	0.00000
3.....	5	5	0.00083	0.00080	—0.00003
4.....	5	5	0.00166	0.00167	+0.00001
5.....	5	5	0.00083	0.00082	—0.00001

Correct results are thus seen to be possible with very small quantities of iodides.

2. The Iodimetric Titration of Iodate formed by the Permanganate Oxidation.

During the study of the permanganate titration of iodides, potassium iodide was added in a number of instances to the solution after the final titration of the excess of ferrous sulfate with permanganate and the resulting iodine titrated with standard thiosulfate. The results obtained

were surprisingly accurate. Consequently the author decided to study the factors influencing this titration.

The first point of interest is naturally the effect of ferric iron on potassium iodide in the acid medium necessary for the liberation of iodine by the interaction of iodic and hydriodic acids.

Tenth-normal potassium iodate (3.5678 g. pure KIO_3 per liter), ferric chloride (1 cc. = 0.006374 g. Fe) slightly acid with hydrochloric acid, ferrous sulfate solution (1 cc. = 0.004528 g. Fe), slightly acid with sulfuric acid, 5 *N* hydrochloric acid, 10 *N* sulfuric acid, 10 *N* phosphoric acid (computed on basis of 3 replaceable hydrogen atoms), manganese preventive solution containing 200 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and 340 cc. H_3PO_4 (sp. gr. 1.7) per liter, *N* potassium iodide, and 0.1055 *N* sodium thiosulfate were used in the experiments of Table V. The letter *s* designates

TABLE V.—REACTION BETWEEN FERRIC IRON AND POTASSIUM IODIDE IN SULFURIC AND PHOSPHORIC ACID SOLUTIONS.

$\text{FeCl}_3 = 0.006374 \text{ g. Fe per cc.}$
 $\text{FeSO}_4 = 0.004528 \text{ g. Fe per cc.}$
 $\text{Na}_2\text{S}_2\text{O}_3 = 0.1055 \text{ N.}$

5 cc. of normal KI solution used in each experiment.

No.	FeCl ₃ Cc.	FeSO ₄ Cc.	0.1 <i>N</i> KIO ₃ Cc.	Normality.			Mn preventive solution. Cc.	Vol. Cc.	Na ₂ S ₂ O ₃ Cc.	Time Min.
				H ₃ PO ₄ .	H ₂ SO ₄ .	HCl.				
1	20	0.5	100	0.10s	10
2	20	1.0	100	0.04s	10
3	20	2.0	100	0.04s	10
4	20	2.0	100	0.04	10
5	20	0.25	200	0.04s	10
6	20	0.125	400	0.04s	20
7	20	0.5	200	0.04s	20
8	20	0.25	400	0.04s	34 ¹
9	20	1.0	.	..	100	5.00	2
10	20	0.25	.	..	400	4.50s	20
11	20	5	100	0.04s	10
12	20	10	100	0.04s	10
13	20	5	200	0.04s	10
14	20	5	400	0.04s	55 ¹
15	20	10	400	0.04s	72 ¹
16	..	50	10	200	0.00s	60
17	..	50 ²	10	200	0.04s	10
18	30	10	200	28.44s	Immediately
19	50	10	200	47.44s	Immediately
20	30	5.0	200	28.44s	Immediately
21	30	5	..	200	28.46s	Immediately
22	30	5	200	28.44s	Immediately
23	20	...	30	5	200	28.46s	Immediately
24	20	...	30	10	200	28.44s	Immediately

¹ At end of 20 minutes starch solution was added and a drop of thiosulfate (0.04 cc.) and the remainder of the time was required for a very faint blue color to reappear.

² Oxidized with permanganate, then 1 cc. of ferrous sulfate was added in excess.

the experiments in which starch was used as indicator. When starch was not used, the bleaching of the iodine color of the solution was taken as the end point.

This series (Experiment 2) shows that normal phosphoric acid is capable of decreasing the speed of reaction between over a tenth of a gram of ferric iron and 0.05 *N* potassium iodide in a volume of 100 cc. at room temperature (21°) to such an extent that it becomes negligible for one or two minutes, only amounting to 0.04 cc. of 0.1 *N* thiosulfate in ten minutes. A considerable increase of the concentration of phosphoric acid, even to 4 *N*, does not change the speed of reaction sufficiently to give a measurable difference of volume of thiosulfate required by the method employed. Dilution of the normal solution to 400 cc. (Experiment 8), thus diminishing the concentration of all the reagents involved, causes a still slower rate of reaction. Sulfuric acid (Experiments 9 and 10) can not be substituted for phosphoric acid, since its action toward decreasing the rate of reaction is not commensurate with the latter. The preventive solution containing phosphoric acid (Experiments 11-15) employed in the permanganate determination of iodides exerts the same influence as phosphoric acid itself. Experiment 16 shows that ferrous iron is without effect. Experiments 18 to 22 show that iodic acid can be titrated quantitatively in the presence of the phosphoric acid or preventive solution, and Experiments 23 and 24 show that the ferric chloride has no influence on the titration of iodic acid, if the titration is performed immediately after adding the potassium iodide.

Definite samples of potassium iodide were taken in the Series VI and varied quantities of potassium bromide and sodium chloride added to each, after which the sample was analyzed for iodine by the permanganate method as previously outlined and the result recorded. Ferrous sulfate solution was then added in slight excess, followed by 5 cc. of *N* KI, and the free iodine titrated immediately with standard thiosulfate adding 1 cc. of 1% starch solution when the solution became very faintly yellow in order to get the sharp iodine-starch end point. The permanganate, ferrous sulfate and thiosulfate solutions used in this series were tenth-normal and the potassium iodide was hundredth-normal.

Table VII includes results obtained using 0.001 *N* solutions. The 0.001 *N* KMnO_4 is thousandth-normal compared with KI as standard. Reacting with iron in acid solution this permanganate would be 0.01 *N* inasmuch as 2KMnO_4 or $\text{K}_2\text{Mn}_2\text{O}_8$ will react with 10 Fe in acid solution but will only oxidize one molecule of KI to KIO_3 in alkaline solution. Hence the permanganate contains 0.316 g. of potassium permanganate per liter. The same relative strength obtains for the ferrous sulfate solution used in this series. The thiosulfate solutions used in this work were standardized against pure potassium iodate, referring the normality

strength of the thiosulfate (0.001 *N*) to potassium iodide as a basis rather than to the iodate. The same precautions used in Series IV are necessary here to avoid any slight impurities of oxidizing or reducing character in the permanganate determination. The manganese solution used in these two series contained 200 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ + 350 cc. of H_3PO_4 (sp. gr. 1.7). In Table VI 15 cc. and in Table VII 5 cc. of this solution were added in each experiment.

TABLE VI.—IODIMETRIC DETERMINATION OF IODIDE IN HALIDE MIXTURES.

	Present—Gram.		Total volume. Cc.	KI—Gram.		
	KBr.	NaCl.		Present.	Found by	
					KMnO ₄ .	Na ₂ S ₂ O ₃ .
1.....	0.5953	0.5851	300	0.0830	0.0828	0.0827
2.....	0.5953	0.5851	300	0.0830	0.0827	0.0826
3.....	0.5953	0.5851	300	0.0830	0.0829	0.0826
4.....	0.5953	0.5851	300	0.0415	0.0414	0.0415
5.....	0.5953	0.5851	250	0.0415	0.0412	0.0415
6.....	0.5953	0.5851	200	0.0166	0.0168	0.0165
7.....	0.5953	0.5851	200	0.0083	0.0082	0.0080
8.....	0.5953	0.5851	200	0.0017	0.0018	0.0016

TABLE VII.—IODIMETRIC DETERMINATION OF SMALL AMOUNTS OF IODIDE IN HALIDE MIXTURES.

	Present—Gram.		Total volume. Cc.	KI—Gram.		
	KBr.	NaCl.		Present.	Found by	
					KMnO ₄ .	Na ₂ S ₂ O ₃ .
1.....	0.0595	0.0585	200	0.00830	0.00825	0.00825
2.....	0.0595	0.0585	200	0.00830	0.00832	0.00826
3.....	0.0595	0.0585	100	0.00415	...	0.00414
4.....	0.0595	0.0585	100	0.00166	0.00169	0.00170
5.....	0.0238	0.0234	100	0.00083	0.00084	0.00086
6.....	0.0238	0.0234	100	0.00033	0.00033	0.00033
7.....	0.0119	0.0117	100	0.00017	0.00017	0.00017

These two series show that the iodimetric titration of the iodate in the residual solution from the permanganate method is accurate if the solution contains sufficient phosphoric acid to prevent the action of ferric iron on potassium iodide. Naturally if the permanganate data are not desired they can be neglected and only the thiosulfate titration computed. The iodimetric method is to be preferred when titrating such small amounts of iodine as the samples of Series VII contained, essentially because of the sharpness of the starch iodine end point contrasted with that of permanganate and of the lesser effect of slight impurities such as oxygen in water on the final titration with the thiosulfate.

The following procedure is well adapted to the analysis of a halogen mixture for its iodine content. One-twentieth to five grams of sample,¹

¹ If as small a sample as 0.05 g. is desired a larger portion should be weighed out and an aliquot analyzed, for example, 0.5 g. diluted to 500 cc. and a 50 cc. portion used in the analysis.

depending upon the amount of iodine present, is dissolved in 100 cc. of recently boiled distilled water in an Erlenmeyer flask, 1 cc. of *N* sodium hydroxide added, the solution is heated to boiling and standard permanganate added, 5–10 cc. at a time with continuous shaking, allowing several seconds between each addition before observing the color of the solution. If the solution becomes cooled it is reheated and the additions are continued until a distinct color (red or green) is imparted to the solution. The flask is covered with a small watch glass and the liquid then heated just below boiling for about five minutes. If the color disappears, more permanganate is added and the solution reheated. It is then cooled in running water and to it is added, all at once, with agitation of the solution, a mixture of 15 cc. of manganese preventive solution (200 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ + 350 cc. H_3PO_4 , of sp. gr. 1.7, per liter) and sufficient standard ferrous sulfate to react with all the manganese dioxide and excess of permanganate and have an excess of ten to fifteen cubic centimeters. As soon as the manganese dioxide has dissolved completely the solution is diluted to 300–400 cc. and titrated with the permanganate¹ to the first appearance of a faint pink color. A smaller amount of preventive solution can be added and a smaller volume used with small quantities of iodine involved. The percentage of iodine is calculated from the amount of permanganate required to oxidize the iodide to iodate.

For the iodimetric titration a few drops of ferrous sulfate are added to bleach out any excess of permanganate, followed by 5 cc. of *N* KI solution (free from iodine) or 1 g. of solid,¹ after which the iodine is titrated immediately with standard thiosulfate. The percentage of iodine or iodide is then computed from the amount of thiosulfate required to react with the iodine produced by the reduction of the iodate to iodide.

The two methods have about equal merit, except when applied to extremely small quantities of iodides, when the iodimetric method is preferable. If the iodimetric method only is to be followed, naturally the strength of the permanganate and ferrous sulfate solutions need not be known exactly.

Summary.

1. In the original method of Pean de St. Gilles for titrating iodide, in the presence of bromide and chloride with permanganate the results are erroneous because of the formation of free bromine, chlorine or hypochlorous acid.

¹ No iodine color should be visible before titration with permanganate or before the addition of potassium iodide prior to the thiosulfate titration. If such a color develops, the proper adjustment has not been made between an exceptionally high concentration of ferric iron and phosphoric acid or too long a time has intervened between the time of finishing the permanganate and starting the thiosulfate titration, in which case another sample must be analyzed, using a greater dilution and correspondingly more preventive solution or phosphoric acid.

2. The presence of manganese sulfate and phosphoric acid in the ferrous solution allows the removal of the excess of permanganate and manganese dioxide without liberation of bromine or chlorine from the halides. Likewise the manganese and phosphoric acid insure a correct permanganate titration of the ferrous iron excess.

3. Iodide can also be determined in the presence of bromide and chloride by addition of potassium iodide to the final solution obtained as in 2 and titration of the liberated iodine with thiosulfate.

4. Both titrations can be made on a single sample, using the residual solution from the permanganate titration for the iodimetric determination.

Very small amounts of iodine are best determined by the iodimetric method. With moderate quantities of iodine both methods outlined are easy of manipulation, rapid in execution and accurate.

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THE PRECIPITATION OF PHOSPHORUS AS AMMONIUM PHOSPHOMOLYBDATE IN THE PRESENCE OF SULFURIC ACID.

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The Neumann method for the determination of phosphorus in organic matter is based upon the oxidation of the material by a mixture of concentrated sulfuric and nitric acids, precipitation of the phosphorus as ammonium phosphomolybdate, and titration of the latter, after removal of ammonia, with standard sodium hydroxide solution. The formula of the phosphomolybdate precipitate has been taken to be essentially $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 2\text{HNO}_3$ under the conditions described by Neumann,¹ Gregerson,² and others. A substance possessing this formula, after the removal of ammonia either by boiling in alkaline solution or by combination with formaldehyde,³ would require 56 equivalents of sodium hydroxide per gram molecule of P_2O_5 to be neutral toward phenolphthalein. If the precipitate is titrated with 0.5 *N* NaOH solution, one cc. would be equivalent to 1.268 mg. P_2O_5 or 0.553 mg. P; on the other hand, if it is dried at 110–120° before titrating, the nitric acid would be driven off and then one cc. would be equivalent to 1.365 mg. P_2O_5 .

The possibility of the composition of the precipitate varying under different conditions has been indicated a number of times,⁴ but the good

¹ *Z. physiol. Chem.*, **37**, 115 (1902); **43**, 35 (1904).

² *Ibid.*, **53**, 453 (1907).

³ Bang, *Biochem. Z.*, **32**, 443 (1911).

⁴ Recently by Hibbard, *J. Ind. Eng. Chem.*, **5**, 998 (1913), who also gives a very complete bibliography. Cf. also A. E. Taylor and C. W. Miller, *J. Biol. Chem.*, **18**, 215 (1914).